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ABSTRACT

Free standing polymer thin films are typically fabricated using a sacrificial interlayer (between the film and its deposition substrate) or overlayer (on top of the film to assist peeling) in order to facilitate removal of the thin film from its deposition substrate. We show the direct delamination and capture of extraordinarily thin (as thin as 8 nm) and large (up to 8 cm) free-standing polymer films. This delamination, without the use of sacrificial materials, is accomplished by engineering the interfacial energy between the film and its substrate. The modification of the substrate is

based on the electrostatic self-assembly of a cationic polyelectrolyte. Eliminating the use of sacrificial materials and instead relying on naturally self-limited assembly makes this method suitable for large areas or very thin films. We have delaminated films with aspect ratios (ratio of lateral dimension between supports to thickness) of 10^7 and captured dry, free-standing films with aspect ratios $>10^6$. Films with an aspect ratio of 10^5 can bear loads up to 10^6 times the mass of the film itself. The presence of the self-assembled layer can be observed using x-ray photoelectron spectroscopy, and this surface modification is persistent through multiple uses. Elimination of sacrificial materials leads to, in this system, an enhancement in the ultimate strength of the thin film. The robustness, persistence, and the self-optimizing nature distinguish this method from various fabrication methods utilizing sacrificial materials and make it a potentially scalable process for the fabrication of ultrathin free-standing or transferrable films for filtration, MEMS, or tissue engineering applications.

Introduction

Free-standing ultra-thin polymer films are important for fundamental polymer science as well as applications in micromachines and sensing,[1 2] catalysis and filtration membranes,[3] and tissue engineering. [4 5] We utilize ultrathin (<100 nm) polymer films as compliant load-bearing elements in inertial confinement fusion targets, which are three-dimensional systems with complex geometries. [6] Our systems require films that stretch across long distances (~5-10 mm) and that can bear an applied load (~2-3 mg). Polymers are useful materials in these and other devices because they can handle large strains before failure, enabling them to conform to applied loads. Free-standing films have been reported to hold up to 70,000 times their own mass. [7] Free-standing films can also be transferred from their deposition substrate to another substrate, such as

a porous support for a filtration membrane or biological tissue for wound healing. [5a] More generally, eliminating substrate effects by fabricating free-standing films is important for measuring thermomechanical properties of polymers confined to two-dimensions. These properties, and their relationship to bulk polymer properties, have been the subject of both fundamental and applied interest. [8]

The most common fabrication process for a free-standing thin film consists of deposition on a substrate, release from the substrate, and capture on a support. The thickness of the film is a limiting factor during film release, because the strain required to delaminate the film increases as the film becomes thinner. To circumvent this problem, a sacrificial interlayer (such as a polymer or polymer composite, [4a, 9] polysaccharide[10] or simple sugar, [9b] or salt[11]) can be deposited between the film and its substrate. After film deposition, the interlayer is dissolved in a suitable solvent and the released film is then captured on a support. A similar process, termed the supporting layer method, deposits a very thick (dozens of microns) sacrificial overlayer on top of the film. [12] The overlayer-film assembly is peeled off the substrate and the sacrificial overlayer is subsequently dissolved in a suitable solvent. Such processes have been used to fabricate free-standing films with aspect ratios of up to 10^6 (film thickness of tens of nm over cm scale widths). [2, 5, 7, 13] Larger aspect ratios are accessible by decreasing the film thickness or by increasing the film area. While the use of sacrificial materials in principle allows very thin films to be fabricated, their use of over large areas presents a number of challenges. For example, the sacrificial interlayer must be optimized to be smooth, uniform, and defect-free over the film area, which becomes challenging for larger areas. Interactions between the sacrificial interlayer may be reflected in the mechanical properties or purity of the final free-standing film. The use of non-aqueous solvents to dissolve the sacrificial layer may also place limitations on subsequent

processing. In the case of the supporting layer method, mechanically peeling over large areas can be impractical.

We address these challenges by eliminating the sacrificial material altogether and instead directly enhancing the release of the film through a pre-deposition substrate modification. An electrostatically-mediated polyelectrolyte self-assembly is used to modify the substrate prior to film deposition. Substrates modified in this fashion can release extraordinarily thin films (8-30 nm) over very large areas (1.5-15 cm). Using this technique, we can delaminate a 10 nm film over 10 cm diameter substrate, an aspect ratio of 10^7. Successful delamination was achieved at the largest substrate size we attempted; larger areas are likely possible with equipment designed to handle larger substrates.

The surface modification has two key characteristics that make it ideally suited for large-area ultrathin films: 1) the chemistry of the modification is chosen based on delamination theory in order to minimize the critical thickness required for film release and 2) the self-assembling nature of the surface modification makes it scalable to large areas without requiring additional process optimization and control. Moreover, the surface modification is entirely water-based, compatible with further aqueous processing, quasi-permanent, and takes only a few minutes. These features make it an attractive and relevant process for scale-up to even larger areas, roll-to-roll processing, or large-volume manufacturing.

Results and discussion

Delamination of a thin film from its substrate spontaneously occurs when the strain energy G_V in the film exceeds the interfacial energy resisting separation γ. This occurs when the film thickness L satisfies the following condition: [14]

$$L > 2\frac{(1+\nu_f)}{(1-\nu_f)}\frac{\gamma}{E\varepsilon^2} \quad \text{(Eq 1)}$$

where L is the film thickness, ν_f is the Poisson's ratio of the film, γ is the difference in interfacial energy between the laminated and delaminated state, E is the Young's modulus of the film, and ε is the strain mismatch between the film and substrate. Thinner films will not delaminate. The only substrate property which appears in Eq. 1 is γ, and reduction of this parameter enables thinner films to delaminate. Note that γ is not the interfacial adhesion energy between the film and its substrate, but rather the energy required to destroy the film-substrate interface and create two new interfaces: the first between the film and its environment and the second between the substrate and its environment. This environment may be air when the film is simply peeled off its substrate, as is the case for thick films (>1 um) and films with an overlying support layer. [5] In the case of peeling, the work required to create the new interfaces can be reduced through the use of a low surface energy substrate such as fluorinated or siloxane polymer. [2]

For ultrathin films without a supporting overlayer or for large-area films, however, peeling is an impractical option since because of the difficulty in maintaining a uniform strain field during peeling. Instead, such films are often released by generating stress in the film by solvent immersion. [15] For a non-swelling substrate such as silicon or glass, the strain mismatch between the film and substrate is $\varepsilon = \xi - 1$, where ξ is the ratio of swollen film thickness to dry film thickness.[16] A low surface energy substrate is not helpful when using this technique with water because the work required to create an interface between the low surface energy substrate and water can actually increase, rather than decrease, γ. Thus, for large-area films removed via water immersion, the ideal substrate modification will reduce interactions (e.g., van der Waals,

covalent, hydrogen) between the film and the substrate while maintaining favorable thermodynamic interactions with water.

This combination of properties is unusual because hydrophilicity is typically associated with chemical moieties (such as hydroxyl groups) that participate in hydrogen bonding. One way to satisfy both requirements is to modify the substrate with a polyelectrolyte. We selected polydiallyldimethylammonium chloride (PDAC), shown in Figure 1, because its quaternary amine side chains are hydrophilic due to their ionic charge but otherwise only participate in van der Waals bonding, provided the film to be released is not electrically charged .

This modification was achieved by allowing positively charged PDAC to electrostatically self-assemble on the negatively charged silicon wafer. Electrostatically-mediated self-assembly of polyelectrolytes is widely used in the fabrication of multilayer thin films, commonly referred to as layer-by-layer (LbL) deposition. In LbL deposition, polyelectrolytes are sequentially adsorbed onto a substrate. [17] Between each deposition step, the substrate is rinsed to remove loosely-bound polyelectrolyte. [18] The substrate modification described in this work can be thought of as the first half-layer in an LbL film. The polycation remaining after deposition and rinse is strongly bound to the negatively charged silicon surface due to proximity-induced cooperativity among the charged side groups. [19] This first half-layer in similar systems is estimated to be 0.5 nm thick, [19-20] which indicates that it is present as a sub-monolayer. The self-limiting nature of the electrostatic assembly process also makes it ideal for use on large-area systems where depositing a uniform and smooth sacrificial layer is challenging. In this study, we deposited a 50 nm PDAC layer on a silicon wafer via spin-coating and then thoroughly rinsed the substrate to remove loosely-bound PDAC as shown schematically in Figure 1.

The polymer used to fabricate the film in this work was a polyvinyl formal resin (PVF), which is sold commercially under the trade names Formvar or Vinylec. The approximate chemical structure of the resin is shown in Figure 2a, with the side chain distribution as reported by the manufacturer.[21] After the substrate modification with PDAC, PVF films were deposited via spin-casting from an ethyl lactate solution. Following a short drying procedure, the deposited films were scored and immersed in a water bath (Figure 2b). The films delaminated from their substrate and floated to the top of the bath, where they were recovered on stainless steel hoops (Figure 2c). Previous fabrication of ultra-thin free-standing PVF films used a commercial surfactant to enhance the release process, [22] though its mechanism of action has never been explained. For comparison, we fabricated films using substrates treated with the commercial surfactant and untreated substrates as well. Treating the deposition substrate with PDAC resulted in a dramatic improvement in the delamination of the PVF thin film. PVF films as thin as 110 nm could be released from an untreated wafer. Films fabricated on substrates treated with the commercial surfactant released easily until 33 nm, beyond which no release was possible. In contrast, films fabricated on substrates treated with PDAC were easily released and successfully captured at thicknesses as low as 8 nm.

This extraordinary enhancement in the delamination properties of the substrate can be understood in the context of the parameter γ in Eq 1. Interfacial adhesive energy for a non-hydrogen bonding epoxy resin to self-assembled monolayers has been measured at up to $\gamma = 700$ mJ/m^2; [23] in our system the PVF is capable of hydrogen bonding with the native silicon oxide surface and this energy is likely higher. [24] Assuming $\gamma \sim 1000\text{-}1500$ mJ/m^2 for PVF on silicon, and estimating $\xi \sim 1.1$ (as measured by dimensional measurement of a bulk sample of PVF), $E \sim 4$ GPa, [21] and $\nu_f \sim 0.25$ for PVF, the minimum thickness for delamination can be estimated with

Eq 1 as 83-125 nm, consistent with the observation that PVF films less than 110 nm do not delaminate from an untreated silicon surface upon water immersion. Whereas hydroxyl groups on the native oxide of the silicon can form hydrogen bonds (up to 30 kJ/mol) with the alcohol side groups of PVF, the quaternary amine moieties of the PDAC limit the interaction between the substrate and polymer film to weak van der Waal's forces (as low as 0.5 kJ/mol). Eliminating hydrogen bonding in favor of van der Waal's interactions reduces γ, and therefore the critical thickness for delamination by a factor of 10-100. These estimates are consistent with the observation that substrates treated with PDAC allow delamination of PVF films more than 10 times thinner than untreated substrates.

The self-assembling, self-limiting nature of the surface modification makes the treatment of large areas simple. There are several reports of free-standing films with aspect ratio ~10^6. [2, 5] Figure 3a shows the delamination of a 30 nm PVF film from a 10 cm diameter silicon wafer, an aspect ratio of 3.3×10^6. Prior to delamination, the film was marked along its perimeter with a black marker to aid the eye. Figure 3b shows a 30 nm free-standing film captured on an 8 cm diameter wire hoop (aspect ratio 2.7×10^6). Even at large diameters, the PVF films retained remarkable strength; Figure 3c shows a 7 cm diameter film mounted on a plastic tube supporting the weight of a 4 g ball more than 30,000 times the mass of the film. No significant changes were made, other than reagent quantities, to self-assemble the PDAC on the silicon across these length scales. The PDAC treatment scales easily to larger sizes; Figure 3d shows a PVF film delaminated from a 15 cm diameter substrate. The ultimate achievable aspect ratio for a free-standing film appears to be limited not by the delamination process, but by the recovery of the free-floating PVF film from the water bath (i.e., the strength of the PVF film) or size considerations (i.e., large-area deposition method for PVF). For example, we successfully

delaminated a 10 nm PVF film from a 10 cm substrate – an aspect ratio of 10^7 – but were unable to remove the film from the water bath without tearing it. PVF films 30 nm and thicker can be removed from the water bath across all the length scales attempted (up to 15 cm).

The presence of the self-assembled PDAC on the substrate was observed spectroscopic ally via X-ray photoelectron spectroscopy (XPS). XPS samples the outermost 1-3 nm of the analyzed surface; [25] such surface sensitivity is necessary due to the fact that the PDAC was present as a sub-monolayer. The atomic composition (as determined by survey scans) of the substrate after PDAC self-assembly is compared to the composition after PVF deposition and delamination in Table 1. The contributions from silicon and oxygen from the underlying substrate have been subtracted; in both cases silicon and oxygen together accounted for around 80% of the atoms. High resolution spectra of the C 1s region are shown in Figure 4. The C 1s region of the substrate after self-assembly of PDAC can be resolved into two peaks, one centered at 284.6 eV and another centered at 285.7 eV. The latter peak is attributable to carbon-nitrogen bonds in the PDAC.[26] The C 1s spectrum after deposition and delamination of PVF is similar. For comparison, reference survey and C 1s spectra of a thick (~50 nm) PDAC layer were also collected.

Nitrogen and chlorine were found in a 1:1 ratio, within experimental uncertainty, for all three samples, in accordance with the molecular structure of PDAC. The presence of the chloride counterion suggests that it plays only a minor role in the charge compensation for the surface-bound polycation, consistent with observations for similar systems. [27] For all three samples, the integrated area of the C-N peak is ~53%, in close agreement with the ratio predicted by the molecular structure (50%). The slight enrichment in carbon (as observed on the survey scans) and peak broadening (as observed in the high-resolution C 1s scans) on the non-reference

samples may be due to a combination of adventitious carbon contributing additional bonding environments and diversity in surface bonding environments due to interactions between the PDAC and the substrate. [28]

The XPS spectra show that PDAC not only adsorbs to the surface, but that it persists after deposition and delamination of PVF. This is important as it shows that PDAC does not act as a sacrificial interlayer during film release. The treatment is robust to the PVF spin casting, which occurs in ethyl lactate solvent, and the delamination procedure, which occurs in water. In fact, a PDAC-treated silicon wafer was used to deposit and release PVF films at least ten times; we found no upper limit to the number of times it could be reused.

A macroscopic (2 mm diameter) ball indenter was used to generate force-deflection curves for equivalent-thickness films fabricated using the PDAC-treated substrates, commercial surfactant treated substrates, and substrates with a sacrificial interlayer. The sacrificial interlayer was an 18 +/1 nm film of sodium polyacrylate. [9b] All the tested films were between 30-35 nm. Representative force versus deflection curves are shown in Figure 5 for all three types of films. The slope of the force-displacement curves is similar for all three fabrication methods (~0.55 g/mm), indicating that all the films had similar elastic and plastic deformation characteristics. However, the ultimate strength of the films was affected by the release method, as seen in Figure 6. Films released from a PDAC modified substrate failed at 40% greater depth (3.4 +/- 0.5 mm, n=3) than those prepared with using the commercial surfactant (2.4 +/- 0.4 mm, n=5). Films released from a sacrificial interlayer were markedly worse than either of the other two (1.5 +/- 0.1 mm, n=3). The ultimate load borne by the strongest film was 1.7 g, which is a remarkable 2.5×10^6 greater than the mass of the film itself.

The exact mechanism of the degraded strength characteristics of the film fabricated using the sacrificial interlayer is unclear, although we hypothesize that it may have been due to acidity of polyacrylic acid formed during the dissolution of the polyacrylate sacrificial layer. We have observed that PVF films exposed to acidic environments display degraded strength characteristics. Such an interaction would not occur on the PDAC-treated substrates; due to the robust binding of the polyelectrolyte to the substrate as observed by XPS, we expect little or no PDAC to enter the delamination water bath.

Conclusions

The delamination and capture of extraordinarily thin and large thin films of PVF can be enhanced by decreasing the interfacial energy between the PVF film and its deposition substrate. Enhancing delamination allows for the elimination of sacrificial materials in the fabrication of these free-standing films, and we have shown that the ultimate strength of the films can be thus enhanced. This may be broadly applicable to other free-standing polymer films as well. The modification relies on electrostatic self-assembly and therefore requires almost no process optimization. The surface modification is persistent as observed spectroscopically and as evidenced by the ability of a modified substrate to be re-used multiple times. The surface modification is also self-limiting, so areas as large as 15 cm were easily treated without additional process optimization. The robustness, persistence, and the self-optimizing nature distinguish this method from various fabrication methods utilizing sacrificial materials. These characteristics make fabrication of free-standing films via enhanced delamination a potentially scalable process for filtration, tissue engineering, MEMs applications.

Experimental

Substrate preparation. All silicon wafers were cleaned in a 100 ^{o}C piranha solution (3 parts H_2SO_4 to 1 part 30 wt% H_2O_2 by volume) and rinsed thoroughly with distilled water prior to use.

PDAC (Sigma-Aldrich, MW 100K-200K) was diluted from the as-received 20 wt% aqueous suspension to 0.5 wt% using distilled water. PDAC was allowed to self-assemble on the silicon wafer by dropping this solution (1-2 mL) onto a silicon wafer and spinning at 4000 rpm for 15 seconds (WS-400 Spin Coater, Laurell technologies). The wafer was dried for 10 seconds on a 100 ^{o}C hot plate, and the presence of PDAC was verified by the characteristic dark grey color of a very thin (<50 nm) transparent film. Loosely-bound PDAC was then removed via thorough rinsing with distilled water; the wafer was then and air dried.

For samples prepared using the commercial surfactant (Windex Foaming Glass Cleaner, SC Johnson), the surfactant was applied to the wafer using the supplied aerosol container, allowed to sit for 1 minute, rinsed thoroughly with distilled water, and air dried.

The sacrificial interlayer was prepared by dissolving PAA (Aldrich Chemical, MW 450K) powder in distilled water to 2 wt%, neutralizing by dropwise addition of 1 M NaOH, and then dilution to 0.5 wt%. The sacrificial layer was made by casting 1-2 mL of this solution onto a clean silicon wafer at 4000 rpm for 15 seconds. The sacrificial layer was 18 +/- 1 nm across the four inch wafer and free of visual defects. Film thickness was measured by spectral reflectometry between 400-1050 nm (F20, FilmMetrics).

Polymer deposition. Polyvinylformal resin (Vinylec E, SPI Supplies) was dissolved to 0.5-2 wt% in ethyl lactate (Sigma-Aldrich, >98%). The solution (1-2 mL) was dropped onto a rotating substrate (~300 rpm) and then spun for 3 seconds at 500-3000 rpm. The weight fraction of PVF

in solution and spin speed was varied depending on the desired film thickness. The film was allowed to dry in place. Remaining solvent was evaporated by drying on a hot plate at 50 ^{o}C for 60 sec. Film thickness was measured on the wafer by spectral reflectometry.

Delamination and mechanical testing. The deposited PVF films were scored in a grid-pattern with a razor blade and slowly immersed in a bath of distilled water at a 40^{o} angle. Individual squares delaminated and floated to the top of the bath where they were captured on a stainless steel hoop-shaped support. For mechanical testing, films were glued onto a 5 mm diameter cylinder and excess film was cut away with a hot soldering iron tip. The mechanical testing apparatus has been previously described in detail. [29] Briefly, the sample was mounted on a balance and films were indented with a 2 mm diameter ruby or stainless steel ball moving at 0.1 mm/min. Large-area films were prepared by skipping the scoring step and instead making small, single score at the edge of the wafer.

XPS characterization. Quantitative compositional analysis of the surface chemistry was performed with XPS using a monochromatic Al Kα source (1486.7 eV). The 200 μm X-ray beam was incident normal to the sample and the detector was 45° from normal. Core-level spectra were collected with pass energy of 23.5 eV with a resolvable XPS peak width of 1.2 eV. Deconvolution of non-resolved peaks was accomplished using Multipak 9.2 (PHI) curve fitting routines with Gaussian-Lorentzian line-shapes and a Shirley background. The collected data were referenced to an energy scale with binding energies for Cu 2p3/2 at 932.72 +/- 0.05 eV and Au 4f7/2 at 84.01 +/- 0.05 eV.

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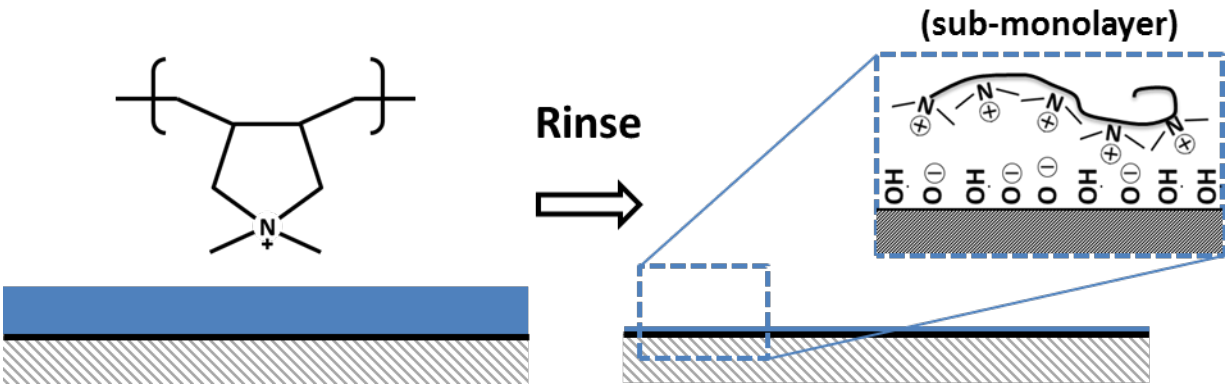

Figure 1. Schematic of the PDAC surface modfication. PDAC (chemical structure shown on left) is first deposited as a ~50 nm film on the surface and then thoroughly rinsed, resulting in a sub-monolayer of strongly-bound PDAC.

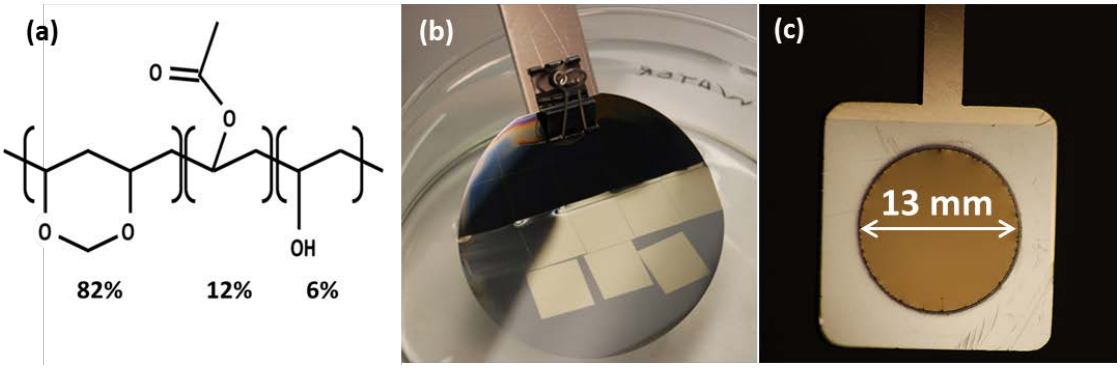

Figure 2. (a) Chemical structure of the PVF resin, with side-chain distribution. (b) Scored PVF films delaminating in the water bath. (c) Free-standing PVF film captured on a stainless steel 13-mm hoop.

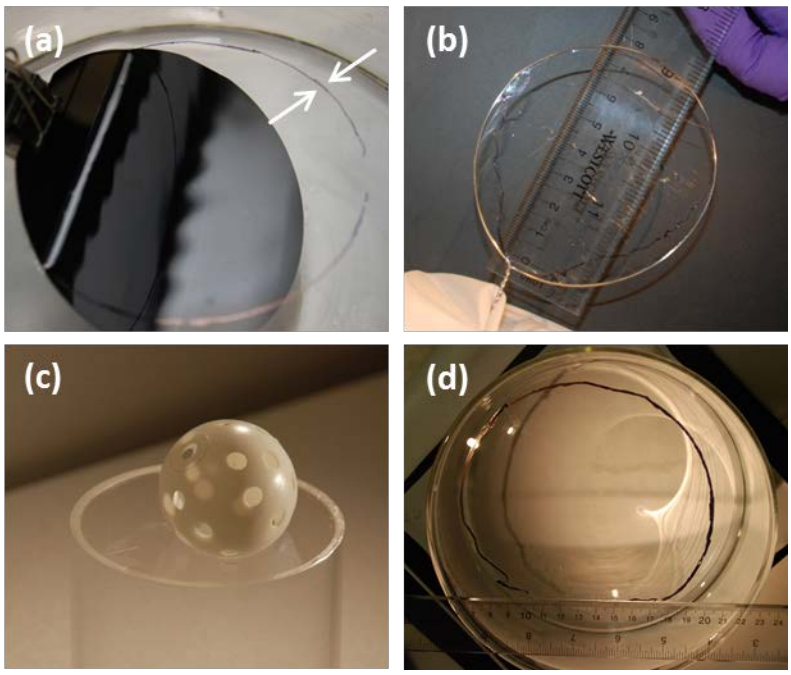

Figure 3. (a) Delamination of a 30 nm PVF film from a 10 cm wafer. The film was marked around its perimeter with a black marker (arrows) prior to delamination to visualize the resultant floating film. (b) 30 nm PVF film captured on an 8 cm wire hoop. (c) 30 nm PVF film mounted on a 7 cm diameter tube supporting a 4 g ball. (d) PVF film delaminated from a 15 cm substrate floating on the top of a water bath. The film was marked around its perimeter with a black marker prior to delamination.

	Assembled[a]	After use[b]	Reference[c]	Ideal[d]
C	87.7%	89.1%	84.5%	80%
N	6.9%	5.5%	8.1%	10%
Cl	5.4%	5.3%	7.4%	10%

Table 1. Atomic compositions of substrate surfaces

a) After self-assembly of PDAC

b) After PVF deposition and delamination

c) PDAC reference sample

d) Ideal composition based on molecular structure

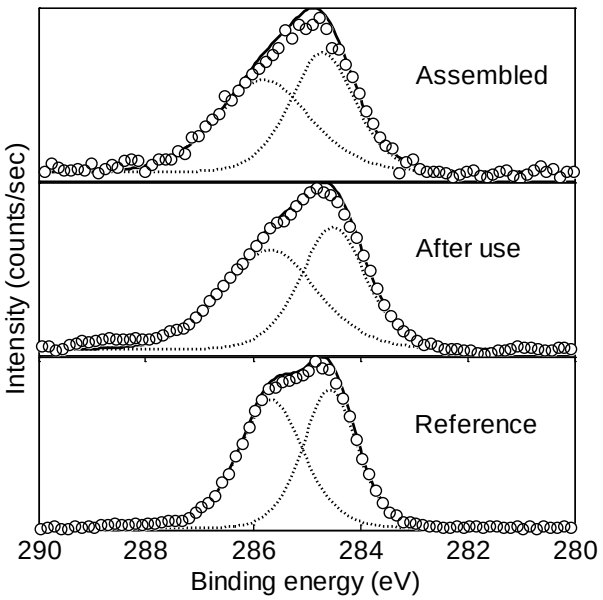

Figure 4. XPS spectra of C 1s region for the substrate after self-assembly of PDAC ("Assembled"), following PVF deposition and delamination ("After use"), and PDAC reference ("Reference"). Open circles represent XPS data. The dashed lines indicate the constituent peaks as determined via peak-fitting (see text) and the solid line is the enveloping curve.

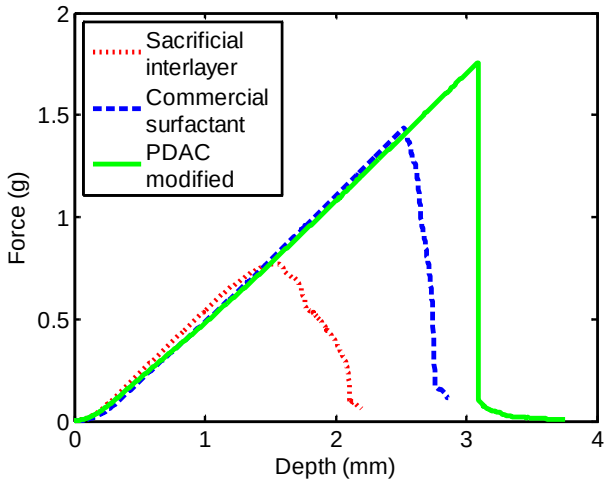

Figure 5. Representative force-deflection curves from the ball indentation test for PVF films released using a sacrificial layer (red dotted line), commericial surfactant (blue dashed line), and PDAC-modified substrate (green solid line).

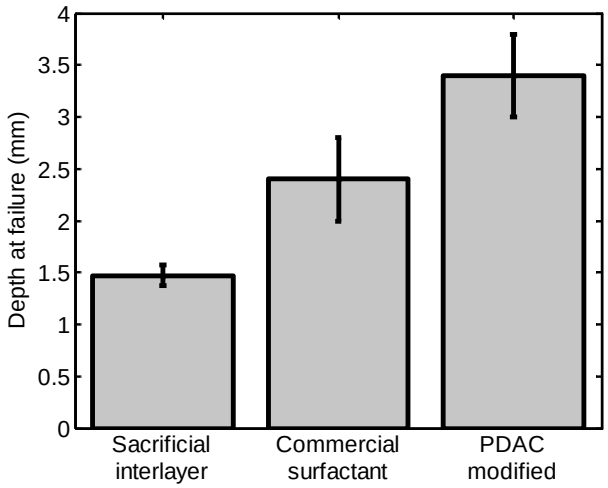

Figure 6. Indentation depth at failure for PVF films released using a sacrificial layer, commercial surfactant, and PDAC-modified substrate.

References

1. (a) Cheng, W.; Campolongo, M. J.; Tan, S. J.; Luo, D., Freestanding ultrathin nano-membranes via self-assembly. *Nano Today* **2009,** *4* (6), 482-493; (b) Matsui, J.; Mitsuishi, M.; Aoki, A.; Miyashita, T., Molecular Optical Gating Devices Based on Polymer Nanosheets Assemblies. *Journal of the American Chemical Society* **2004,** *126* (12), 3708-3709.
2. Greco, F.; Zucca, A.; Taccola, S.; Menciassi, A.; Fujie, T.; Haniuda, H.; Takeoka, S.; Dario, P.; Mattoli, V., Ultra-thin conductive free-standing PEDOT/PSS nanofilms. *Soft Matter* **2011,** *7* (22), 10642-10650.
3. Ulbricht, M., Advanced functional polymer membranes. *Polymer* **2006,** *47* (7), 2217-2262.
4. (a) Sreenivasan, R.; Bassett, E. K.; Hoganson, D. M.; Vacanti, J. P.; Gleason, K. K., Ultra-thin, gas permeable free-standing and composite membranes for microfluidic lung assist devices. *Biomaterials* **2011,** *32* (16), 3883-3889; (b) Wan, L.-S.; Liu, Z.-M.; Xu, Z.-K., Surface engineering of macroporous polypropylene membranes. *Soft Matter* **2009,** *5* (9), 1775-1785.
5. (a) Fujie, T.; Matsutani, N.; Kinoshita, M.; Okamura, Y.; Saito, A.; Takeoka, S., Adhesive, Flexible, and Robust Polysaccharide Nanosheets Integrated for Tissue-Defect Repair. *Advanced Functional Materials* **2009,** *19* (16), 2560-2568; (b) Okamura, Y.; Kabata, K.; Kinoshita, M.; Saitoh, D.; Takeoka, S., Free-Standing Biodegradable Poly(lactic acid) Nanosheet for Sealing Operations in Surgery. *Advanced Materials* **2009,** *21* (43), 4388-4392.
6. (a) Haan, S. W.; Atherton, J.; Clark, D. S.; Hammel, B. A.; Callahan, D. A.; Cerjan, C. J.; Dewald, E. L.; Dixit, S.; Edwards, M. J.; Glenzer, S.; Hatchett, S. P.; Hicks, D.; Jones, O. S.; Landen, O. L.; Lindl, J. D.; Marinak, M. M.; MacGowan, B. J.; MacKinnon, A. J.; Meezan, N. B.; Milovich, J. L.; Munro, D. H.; Robey, H. F.; Salmonson, J. D.; Spears, B. K.; Suter, L. J.; Town, R. P.; Weber, S. V.; Kline, J. L.; Wilson, D. C., NIF IGNITION CAMPAIGN TARGET PERFORMANCE AND REQUIREMENTS: STATUS MAY 2012. *Fusion Science and Technology* **2013,** *63* (2), 67-75; (b) Haan, S. W.; Lindl, J. D.; Callahan, D. A.; Clark, D. S.; Salmonson, J. D.; Hammel, B. A.; Atherton, L. J.; Cook, R. C.; Edwards, M. J.; Glenzer, S.; Hamza, A. V.; Hatchett, S. P.; Herrmann, M. C.; Hinkel, D. E.; Ho, D. D.; Huang, H.; Jones, O. S.; Kline, J.; Kyrala, G.; Landen, O. L.; MacGowan, B. J.; Marinak, M. M.; Meyerhofer, D. D.; Milovich, J. L.; Moreno, K. A.; Moses, E. I.; Munro, D. H.; Nikroo, A.; Olson, R. E.; Peterson, K.; Pollaine, S. M.; Ralph, J. E.; Robey, H. F.; Spears, B. K.; Springer, P. T.; Suter, L. J.; Thomas, C. A.; Town, R. P.; Vesey, R.; Weber, S. V.; Wilkens, H. L.; Wilson, D. C., Point design targets, specifications, and requirements for the 2010 ignition campaign on the National Ignition Facility. *Physics of Plasmas* **2011,** *18* (5).
7. Vendamme, R.; Onoue, S. Y.; Nakao, A.; Kunitake, T., Robust free-standing nanomembranes of organic/inorganic interpenetrating networks. *Nature Materials* **2006,** *5* (6), 494-501.
8. (a) Alcoutlabi, M.; McKenna, G. B., Effects of confinement on material behaviour at the nanometre size scale. *Journal of Physics-Condensed Matter* **2005,** *17* (15), R461-R524; (b) Ellison, C. J.; Torkelson, J. M., The distribution of glass-transition temperatures in nanoscopically confined glass formers. *Nature Materials* **2003,** *2* (10), 695-700; (c) Priestley, R. D.; Ellison, C. J.; Broadbelt, L. J.; Torkelson, J. M., Structural relaxation of polymer glasses at surfaces, interfaces and in between. *Science* **2005,** *309* (5733), 456-459; (d) Si, L.; Massa, M. V.; Dalnoki-Veress, K.; Brown, H. R.; Jones, R. A. L., Chain entanglement in thin freestanding polymer films. *Physical Review Letters* **2005,** *94* (12); (e) Torres, J. M.; Stafford, C. M.; Vogt, B.

D., Elastic Modulus of Amorphous Polymer Thin Films: Relationship to the Glass Transition Temperature. *Acs Nano* **2009,** *3* (9), 2677-2685.
9. (a) Dubas, S. T.; Farhat, T. R.; Schlenoff, J. B., Multiple Membranes from "True" Polyelectrolyte Multilayers. *Journal of the American Chemical Society* **2001,** *123* (22), 5368-5369; (b) Linder, V.; Gates, B. D.; Ryan, D.; Parviz, B. A.; Whitesides, G. M., Water-soluble sacrificial layers for surface micromachining. *Small* **2005,** *1* (7), 730-736; (c) Ono, S. S.; Decher, G., Preparation of Ultrathin Self-Standing Polyelectrolyte Multilayer Membranes at Physiological Conditions Using pH-Responsive Film Segments as Sacrificial Layers. *Nano Letters* **2006,** *6* (4), 592-598.
10. Mamedov, A. A.; Kotov, N. A., Free-Standing Layer-by-Layer Assembled Films of Magnetite Nanoparticles. *Langmuir* **2000,** *16* (13), 5530-5533.
11. Lee, H. J.; Lee, S. W.; Goto, H.; Lee, S. H.; Lee, H. J.; Ha, J. S.; Goto, T.; Cho, M. W.; Yao, T.; Hong, S. K., Self-separated freestanding GaN using a NH4Cl interlayer. *Applied Physics Letters* **2007,** *91* (19).
12. Stroock, A. D.; Kane, R. S.; Weck, M.; Metallo, S. J.; Whitesides, G. M., Synthesis of Free-Standing Quasi-Two-Dimensional Polymers. *Langmuir* **2002,** *19* (6), 2466-2472.
13. Nardin, C.; Winterhalter, M.; Meier, W., Giant Free-Standing ABA Triblock Copolymer Membranes. *Langmuir* **2000,** *16* (20), 7708-7712.
14. Freund, L. B.; Suresh, S., *Thin Film Materials: Stress, Defect Formation and Surface Evolution*. Cambridge University Press: 2003.
15. Buck, M. E.; Lynn, D. M., Free-Standing and Reactive Thin Films Fabricated by Covalent Layer-by-Layer Assembly and Subsequent Lift-Off of Azlactone-Containing Polymer Multilayers. *Langmuir* **2010,** *26* (20), 16134-16140.
16. Fu, T. Z.; Durning, C. J.; Tong, H. M., SIMPLE-MODEL FOR SWELLING-INDUCED STRESSES IN A SUPPORTED POLYMER THIN-FILM. *Journal of Applied Polymer Science* **1991,** *43* (4), 709-721.
17. (a) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R., Ultrathin polymer coatings by complexation of polyelectrolytes at interfaces: suitable materials, structure and properties. *Macromolecular Rapid Communications* **2000,** *21* (7), 319-348; (b) Decher, G., Fuzzy nanoassemblies: Toward layered polymeric multicomposites. *Science* **1997,** *277* (5330), 1232-1237; (c) Hammond, P. T., Form and Function in Multilayer Assembly: New Applications at the Nanoscale. *Advanced Materials* **2004,** *16* (15), 1271-1293.
18. Guzman, E.; Ritacco, H.; Rubio, J. E. F.; Rubio, R. G.; Ortega, F., Salt-induced changes in the growth of polyelectrolyte layers of poly(diallyl-dimethylammonium chloride) and poly(4-styrene sulfonate of sodium). *Soft Matter* **2009,** *5* (10), 2130-2142.
19. Kriz, J.; Dybal, J.; Kurkova, D., Cooperativity in macromolecular interactions as a proximity effect: NMR and theoretical study of electrostatic coupling of weakly charged complementary polyions. *Journal of Physical Chemistry B* **2003,** *107* (44), 12165-12174.
20. Krogman, K. C.; Zacharia, N. S.; Schroeder, S.; Hammond, P. T., Automated Process for Improved Uniformity and Versatility of Layer-by-Layer Deposition. *Langmuir* **2007,** *23* (6), 3137-3141.
21. Applications for polyvinyl acetal resins: Developments from Monsanto. *Pigment & Resin Technology* **1993,** *15* (9), 13-18.
22. Stadermann, M.; Letts, S. A.; Bhandarkar, S., IMPROVEMENTS TO FORMVAR TENT FABRICATION USING THE MENISCUS COATER. *Fusion Science and Technology* **2011,** *59* (1), 58-62.

23. Zhuk, A. V.; Evans, A. G.; Hutchinson, J. W.; Whitesides, G. M., The adhesion energy between polymer thin films and self-assembled monolayers. *Journal of Materials Research* **1998,** *13* (12), 3555-3564.
24. Chapman, B. N., Thin-film adhesion. *Journal of Vacuum Science and Technology* **1974,** *11* (1), 106-113.
25. Grant, J. T.; Briggs, D., *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*. IM Publicatoins: Chichester, United Kingdom, 2003.
26. Beamson, G.; Briggs, D., *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*. John Wiley & Sons Ltd: West Sussex, England, 1992; p 274.
27. (a) Lourenço, J. M. C.; Ribeiro, P. A.; Botelho do Rego, A. M.; Braz Fernandes, F. M.; Moutinho, A. M. C.; Raposo, M., Counterions in Poly(allylamine hydrochloride) and Poly(styrene sulfonate) Layer-by-Layer Films. *Langmuir* **2004,** *20* (19), 8103-8109; (b) Riegler, H.; Essler, F., Polyelectrolytes. 2. Intrinsic or Extrinsic Charge Compensation? Quantitative Charge Analysis of PAH/PSS Multilayers. *Langmuir* **2002,** *18* (17), 6694-6698.
28. Wallart, X.; Henry de Villeneuve, C.; Allongue, P., Truly Quantitative XPS Characterization of Organic Monolayers on Silicon: Study of Alkyl and Alkoxy Monolayers on H−Si(111). *Journal of the American Chemical Society* **2005,** *127* (21), 7871-7878.
29. (a) Kucheyev, S. O.; Stadermann, M.; Shin, S. J.; Satcher, J. H.; Gammon, S. A.; Letts, S. A.; van Buuren, T.; Hamza, A. V., Super-Compressibility of Ultralow-Density Nanoporous Silica. *Advanced Materials* **2012,** *24* (6), 776-780; (b) Stadermann, M.; Kucheyev, S. O.; Lewicki, J.; Letts, S. A., Radiation tolerance of ultra-thin Formvar films. *Applied Physics Letters* **2012,** *101* (7), 071908-3.